

## PATENT ABSTRACTS OF JAPAN

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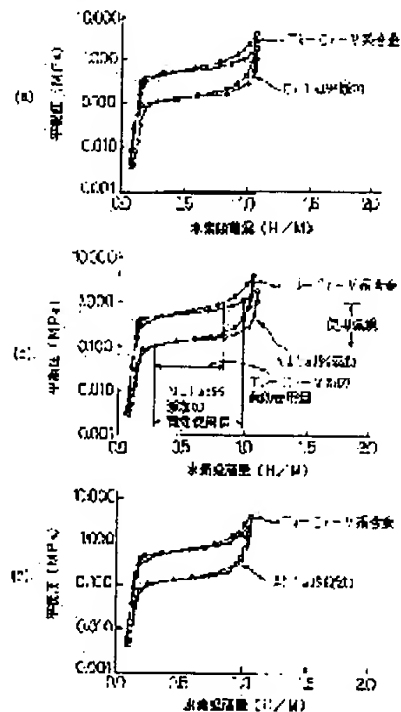
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## (54) HYDROGEN STORAGE ALLOY EXCELLENT IN PLATEAU FLATNESS

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a hydrogen storage alloy improved in plateau flatness, widen in using environments and furthermore excellent in occluding and releasing characteristics, as to a hydrogen storage alloy excellent in plateau flatness, particularly the one in which a fourth element is added to a Ti-Cr-V series, by forming its metallic structure of the one of the BCC single phase or converting it into the one of BCC single phase by heat treatment.

SOLUTION: In an alloy expressed by the general formula of  $Ti_a Cr_b V_c Ad$  with the ratios of numbers of atoms as (a), (b), (c) and (d), where  $a+b+c+d=100$ , (A) denotes one or  $\geq$  two kinds among the group IIIb, Mn, Co, Ni, Zr, Nb, Hf, Ta and Al, and, also, compositional regions of  $14 \leq a \leq 60$ ,  $14 \leq b \leq 60$ ,  $9 \leq c \leq 60$  and  $0 < d < 8$  or  $9 \leq c \leq 25$  are regulated and having a structure of BCC (body-centered cubic) + C14 (Laves phase), it is heated at 1000 to 1400°C and is rapidly cooled to convert its structure into the one of the BCC single phase.



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CLAIMS

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[Claim(s)]

[Claim 1] It is a general formula  $Tia CrbVc Ad$  as atomic ratios  $a, b, c,$  and  $d$ . It is the hydrogen storing metal alloy which is expressed, however is characterized by for  $a+b+c+d=100$  and  $A$  being a kind of an IIIb group, and Mn, Co, nickel, Zr, Nb, Hf, Ta and aluminum, or two sorts or more, and being  $14 \leq a \leq 60, 14 \leq b \leq 60, 9 \leq c \leq 60,$  and  $0 < d < 8$ .

[Claim 2] It is a general formula  $Tia CrbVc Ad$  as atomic ratios  $a, b, c,$  and  $d$ . It is expressed. However,  $a+b+c+d=100$  and  $A$  are a kind of an IIIb group, and Mn, Co, nickel, Zr, Nb, Hf, Ta and aluminum, or two sorts or more, and are the composition field of  $14 \leq a \leq 60, 14 \leq b \leq 60, 9 \leq c \leq 25,$  and  $0 < d < 8$ . The hydrogen storing metal alloy characterized by for the crystal structure heating and quenching at 1000-1400 degrees C in the alloy which is BCC(body center cube)+C14 (Laves phase), and performing heat treatment which carries out haptosis to a BCC phase.

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] About the hydrogen storing metal alloy excellent in plateau flat nature, this invention is what added the 4th element especially in the Ti-Cr-V system, and relates to the hydrogen storing metal alloy which has improved plateau flat nature, and lost restrictions of an operating environment, and was excellent in occlusion and the emission characteristic by carrying out BCC haplois of the metal texture with BCC single phase or heat treatment.

[0002]

[Description of the Prior Art] From a viewpoint of global environment problems, reuse of solar heat, atomic power, hydraulic power, a wind force, heat of the earth, and waste heat etc. is proposed as new energy replaced with a fossil fuel. However, how in any case, the energy is stored and conveyed poses a common problem. Water is electrolyzed using solar heat or hydraulic power, and the system using the hydrogen obtained by this as an energy medium can be called ultimate clean energy in that a raw material is water and the product which consumes energy and can do it is water again.

[0003] or [ that occlusion of the hydrogen gas of about 1000 times or more of own volume of an alloy is carried out, a hydrogen storing metal alloy can store it as a storage / transportation means of this hydrogen, and the volume density is almost equivalent to a liquid or solid-state hydrogen ] -- or it is more than it LaNi<sub>5</sub> by which the metal of body centered cubic structures (BCC structure is called below), such as V, Nb, Ta, and a Ti-V alloy, is already put in practical use as this hydrogen-absorption material etc. -- AB<sub>5</sub> A type alloy and TiMn<sub>2</sub> etc. -- AB<sub>2</sub> Compared with the type alloy, carrying out occlusion of a lot of hydrogen was known for many years. This is because there are many hydrogen-absorption sites in the crystal lattice and the hydrogen storage capacity by calculation is very as large as H/M=2.0 (alloys, such as Ti, V, etc. which are about 50 atomic weight, about 4.0 wt(s)%) with BCC structure.

[0004] In a pure vanadium alloy, occlusion of the almost same about 4.0 wt(s)% as the value calculated from the crystal structure is carried out, and the abbreviation half is emitted under an ordinary temperature ordinary pressure. It is known that big hydrogen storage capacity and a good hydrogen-desorption property are similarly shown in 5A group's Nb and Ta of an element of the same periodic table. In pure metals, such as V, Nb, and Ta, since cost is very high, in the industrial application which needs a certain amount of amounts of alloys, such as a hydrogen tank and an nickel-MH cell, it is not realistic. Then, the property has been investigated in the alloy of the component range which has BCC structures, such as Ti-V. However, with these BCC alloys, the reaction rate made into the problem also in V, Nb, and Ta is slow, and, in addition to the point of difficulty, activation has also produced new troubles, like there are few burst sizes only by carrying out occlusion in the practical temperature and pressure. The alloy which makes a BCC phase a main composition phase as this result has not yet resulted in practical use.

[0005] A plateau field is not flat, and since the hysteresis is large, on the other hand, harnessing a material property with the conventional Ti-Cr-V system alloy, depending on an operating environment, although it has the hydrogen-absorption property of high capacity can be being finished. the alloy with the small hysteresis which added a kind which are Co, Cu, Nb, rare earth elements, and Zr, or two sorts to JP,61-25013,A as well-known technology of this field at Ti, Cr, and V is indicated However, when a plateau field is not flat, harnessing the property of a hydrogen storing metal alloy cannot fully be finished, and there is a problem that the amount of effective [ used ] of hydrogen is small.

[0006]

[Problem(s) to be Solved by the Invention] The purpose of this invention is for the addition ratio of Ti, Cr, and V to offer the hydrogen storing metal alloy which examines adding the 4th element into a Ti-Cr-V system alloy, and can

carry out flattening of the plateau to it, without changing. Other purposes of this invention consider the composition which can carry out BCC haplosis of the organization of the aforementioned 4 yuan system alloy, and are to the thing of 2 phase mixing zone of C14 and BCC to offer a hydrogen storing metal alloy with the aforementioned flat plateau as BCC haplosis with heat treatment.

[0007] From the concrete data about an improvement of the hydrogen absorption and the emission characteristic in the aforementioned 4 yuan system alloy, plateau flat nature, and a hysteresis, another purpose of this invention is to offer the hydrogen storing metal alloy which can demonstrate a material property to the maximum extent without limiting an operating environment.

[0008]

[Means for Solving the Problem] The above-mentioned purpose is a general formula  $Ti_a Cr_b V_c Al_d$  as atomic ratios  $a, b, c,$  and  $d$ . It is attained by the hydrogen storing metal alloy which is expressed, however is characterized by for  $a+b+c+d=100$  and  $A$  being a kind of an IIb group, and Mn, Co, nickel, Zr, Nb, Hf, Ta and aluminum, or two sorts or more, and being  $14 \leq a \leq 60, 14 \leq b \leq 60, 9 \leq c \leq 60,$  and  $0 < d < 8$ .

[0009] Moreover, the above-mentioned purpose is a general formula  $Ti_a Cr_b V_c Al_d$  as atomic ratios  $a, b, c,$  and  $d$ . It is expressed. However,  $a+b+c+d=100$  and  $A$  are a kind of an IIb group, and Mn, Co, nickel, Zr, Nb, Hf, Ta and aluminum, or two sorts or more, and are the composition field of  $14 \leq a \leq 60, 14 \leq b \leq 60, 9 \leq c \leq 25,$  and  $0 < d < 8$ . The crystal structure heats and quenches at 1000-1400 degrees C in the alloy which is BCC(body center cube)+C14 (Laves phase), and it is attained by the hydrogen storing metal alloy characterized by performing heat treatment which carries out haplosis to a BCC phase.

[0010]

[Embodiments of the Invention] In order to have a property as a hydrogen storing metal alloy which was excellent by considering as BCC structure and to improve plateau flat nature while the Ti-Cr-V system which is a BCC metal holds the property of the big hydrogen storage capacity which it has structurally from much old experiments namely, an artificer etc. acquires the knowledge that it is effective that predetermined carries out amount addition of the 4th element, and attains this invention based on this.

[0011] In composition of this invention, it becomes a BCC phase or BCC phase +C14 phase like the after-mentioned. Since it is made to BCC-ize with heat treatment in the case of BCC phase +C14 phase, it heated and quenched at 1000-1400 degrees C (2 hours or more are desirable), and the BCC phase has been formed by performing heat treatment which carries out haplosis to a BCC phase. Consequently, while hydrogen storage capacity is large, plateau flat nature improves by addition of the 4th element, and an alloy with the high amount of effective [ used ] as an alloy is especially obtained by this plateau flat disposition top. From the first, also in the component range of BCC single phase, since an effect is in homogenization, heat-treating is not heat treatment only on a plateau flat disposition, and these improvement effects are discovered simultaneously.

[0012] With the conventional BCC type and a Ti-Cr-V alloy, it cannot but become low weighted solidity, without reaching the property which material has, when the operating environment (temperature, pressure) of an alloy is limited, since an inclination exists in a plateau. It becomes impossible to make the hydrogen which carried out occlusion that occlusion cannot be carried out from this to the amount of hydrogen which an alloy has, and in which occlusion is possible, and at once emit completely.

[0013] Next, the technical feature and the reason for limitation of this invention are explained. The 1st invention made  $A$  a kind of an IIb group, and Mn, Co, nickel, Zr, Nb, Hf, Ta and aluminum, or two sorts or more as the 4th element for these components influencing plateau flat nature greatly like drawing 1. Ce etc. is sufficient, although Y and a lanthanoids are desirable and especially Y and La are desirable in an IIb group. Drawing 1 (a) shows Co to the Ti-Cr-V system, and, as for drawing 1 (b), drawing 1 (c) shows the PCT (hydrogen \*\*\*\*\* ) curve at the time of adding [ nickel ] one ateach % for aluminum in a Ti-Cr-V system to the Ti-Cr-V system. As it is indicated in drawing 2 as the plateau flat nature of this invention, with Co addition alloy, it is decreasing at 7.5 (L1) degrees to the plateau inclination (L2) of the occlusion line of a base alloy being 13.5 degrees. The value (L1/L2) 7.5 of the ratio in this case / 13.5= 0.556 is expressed as a relative value of plateau flat nature. On the other hand, expressing with  $H_f = (\text{absorption-pressure force } P_a \text{ in occlusion mean value}) / (\text{desorption pressure force } P_d \text{ in a discharge mean value})$  estimates a hysteresis factor ( $H_f$ ).

[0014] For example, since plateau flat nature is improved like drawing 1 (b), the amount of effective [ used ] of hydrogen increases. Moreover, a hysteresis can be made small and the amount of repeats of the hydrogen absorption and discharge in the case of actually using it increases from there being few restrictions by the operating environment and the capacity fully being demonstrated. Drawing 3 summarizes the addition effect (1at%) of the 4th element shown in the below-mentioned example. In this drawing, plateau flat nature and a vertical axis are plotted for a horizontal axis as a hysteresis factor by making the conventional Ti-Cr-V system alloy into a standard. This

drawing shows that an effect is large especially from nickel, Co, and Mn as the 4th element.

[0015] As an addition, it is a general formula  $Ti_aCr_bV_cAd$  as atomic ratios  $a$ ,  $b$ ,  $c$ , and  $d$ . It is expressed, however is  $a+b+c+d=100$ . Having specified to  $14 \leq a \leq 60$ ,  $14 \leq b \leq 60$ ,  $9 \leq c \leq 60$ , and  $0 < d < 8$  If  $c$  is  $c \geq 60$ , only by adjustment of a Ti/Cr ratio, it becomes difficult [ plateau oppression \*\* ], and when  $a$  is 60 \*\*, plateau \*\* will fall remarkably, and when  $b$  is 60 \*\*, plateau \*\* will become remarkably high. When  $a$  and  $b$  are furthermore less than 14, respectively, BCC-ization by heat treatment becomes difficult. On the other hand, about  $d$ , when  $d$  is  $d > 8$ , plateau flat nature will deteriorate rather than the original 3 yuan system alloy. Moreover, when  $d$  decreases from 8, the improvement effect of flat nature also becomes small in proportion to it.

[0016] Drawing 4 shows boundary composition of BCC which is the 3 yuan state diagram of a Ti-Cr-V system, and shows the fundamental feature of this invention, and BCC+C14 phase, C14 exists in a Ti-Cr system side, and 2 phase field exists in this circumference. It is necessary to become 2 phase coexistence of BCC+C14 and to carry out BCC haplosis with subsequent heat treatment in [ composition ]  $9 \leq c \leq 25$ , at an atomic ratio. Moreover, in  $c < 9$ , since the haplosis of BCC becomes difficult even if it heat-treats, it has excepted.

[0017] Next, the hydrogen \*\*\*\*\* of this invention hydrogen storing metal alloy is explained. First, like the above, the basic alloy system of this invention is a Ti-Cr-V system, and adds the 4th element to this. Therefore, as a property of an alloy, this fundamental system is inherited and contrast with this can explain. It is surmised by the sludge which deposits in a BCC phase grain boundary decreasing, and promoting BCC-ization by addition of the 4th element of the above, that it has led to the improvement of a hydrogen-desorption property.

[0018] An operation of heat treatment of this invention is considered still as follows. The lattice strain produced in the interface of a two phase as mentioned above changes the distribution state of hydrogenation distortion produced according to hydrogenation. Especially, in the alloy of BCC structure like this invention, distortion produced according to hydrogenation has big influence on hydrogen absorption and the pressure differential (hysteresis) of discharge. In the alloy which has the fine structure like this invention, it becomes possible by controlling such an early distortion by heat treatment to make the optimal small strain distribution of a hysteresis.

[0019] In this invention, heat treatment temperature becomes difficult to get at less than 1000 degrees C, and, on the other hand, in 1400-degree-C \*\*, the effect is heat. Moreover, as heat treatment time, a treatment effect is inadequate in less than 1 minute, and it is 100. It is in the inclination for a treatment effect to be saturated, and \*\*\*\*\* is enough less than [ this ]. Moreover, as cooling processing, it is preferably good at hardening processing. Moreover, solution treatment is homogenization and homonymy, when you may combine with an aging treatment and this aging treatment is not taken. this invention is explained in full detail based on an example below.

[0020]

[Example]

without it changes the Ti/Cr/V ratio of a base alloy on the following conditions as an example of example 1 this invention -- the 4th element X -- 1at% -- as a property [ in / the operating environment (0 degree-C ten atmospheric pressure of hydrogen restoration, 40 degrees-C one atmospheric pressure of hydrogen desorption) of FCEV (fuel cell electric vehicle) / it adds and ] -- hydrogen \*\*\*\*\* -- especially, measurement of plateau flat nature and a hysteresis factor was performed, and structural analysis and the organization were investigated further

[0021]

Base alloy composition: Ti26.5Cr33.5V 40.0 sample-offering alloy composition : About 20g ingot performed by the arc dissolution in an argon they are [ dissolution ] Ti26.24 Cr 33.17V39.60Al.00, A=Y, and La, Zr, Hf, Nb, Ta, Mn, Co, nickel and aluminum and for which all the samples of this example used water-cooled copper Haas. All the data of this example ground the ingot [ having cast ] in air, and heat-treated by carrying out Ar enclosure (200 - 300Torr) to a quartz tube (after [ 1200 degree-Cx2hr ] water quenching). As activation, they are 500 degrees C and 10-4torr vacuum length +50atm. After carrying out the four-cycle loop of the hydrogen pressurization and performing it, the hydrogen storage capacity and \*\*\*\*\* of an alloy are performed by the PCT measurement based on the vacuum condition specified for the pressure composition constant-temperature-line measuring method (JIS H7201) by the constant volume method. Moreover, transmission-electron-microscope observation produced the thin film by ion milling from the sample of bulk.

[0022] Moreover, structural analysis of an alloy was performed using EDX (energy-dispersion type X diffraction) of a transmission electron microscope and attachment. The crystal structure model was created based on the information furthermore acquired with the transmission electron microscope, and lied belt analysis of powder X diffraction data was performed. Lied belt analysis can be asked for the weight fraction of each phase by calculation while it can carry out [ precise ]-izing of the crystal structure parameter using diffraction intensity unlike the usual X-ray diffraction method.

[0023] Analysis soft RIETAN94 which the National Institute for Research in Inorganic Materials spring doctor

developed was used for lied belt analysis. Although the phase molar fraction and crystal structure parameter as an average are obtained with a sufficient precision, for the analysis, a fairly probable crystal structure model is required of lied belt analysis. drawing 5 - drawing 14 -- as a measurement result of this example, hydrogen storage capacity is shown in a horizontal axis, and an parallel pressure shows each for a PCT property to a vertical axis here -- drawing 5 -- the aforementioned base alloy and this -- Co1at% -- the property about the added alloy is shown. Similarly, drawing 6 - drawing 14 show each of the PCT curve about what added 1at% of the following nickel, aluminum, Y, La, Zr, Hf, Ta, Mn, and Nb like drawing 5. As compared with the base alloy, improvement in the hydrogen storage capacity as hydrogen \*\*\*\*\*, Prato flat nature, and a hysteresis factor was accepted from these drawings by 4th element 1at% of addition.

[0024] Next, each is shown for the energy-dispersion type X diffraction result used for structural analysis about Co, nickel, and aluminum addition alloy in drawing 15 (a) - (c). The peak which was well in agreement with the peak position peculiar to BCC structure also in the chart of which alloy was accepted. furthermore, the microstructure of a base alloy -- as 100 times of drawing 16 (a), and the 500 time photograph of 16 (b) -- nickel -- 1at% -- the microstructure photograph of the added alloy is shown as 100 times of drawing 16 (c), and a 500 time photograph of 16 (d). By addition of the 4th element, a new organization does not appear at all, but the organization of a base alloy is improved further, and this photograph shows that it is in the inclination which decreases a two phase field.

[0025] Example 2 this example considers change of hydrogen \*\*\*\*\* by composition of an alloy content. the base alloy of a Ti-Cr-V system alloy -- the 4th element -- adding -- A=0.5 and 1. -- it adjusts to the following component (No. \*\*-\*\*) so that it may become 0, 5.0, and 8.0at(s)%

\*\* Ti15.0Cr34.7V49.8A0.5 (this invention)  
 \*\* Ti34.7Cr15.0V49.8A0.5 (this invention)  
 \*\* Ti26.2Cr33.2V39.6A1.0 (this invention)  
 \*\* Ti47.5Cr28.5V19.0A5.0 (this invention)  
 \*\* Ti28.5Cr47.5V19.0A5.0 (this invention)  
 \*\* Ti25.0Cr35.0V32.0A8.0 (example of comparison : outside of a claim)

[0026] Here, about 20g ingot performed all of A=Co, nickel, aluminum, Y, La, Zr, Hf, Ta and Mn, and the sample of this example by the arc dissolution in an argon which used water-cooled copper Haas. All the data of this example ground the ingot [ having cast ] in air, and heat-treated by carrying out Ar enclosure (200 - 300Torr) to a quartz tube (after [ 1200 degree-Cx2hr ] water quenching). As activation, they are 500 degrees C and 10-4torr vacuum length +50atm. After carrying out the four-cycle loop of the hydrogen pressurization and performing it, the hydrogen storage capacity and \*\*\*\*\* of an alloy are performed by the PCT measurement based on the vacuum condition specified for the pressure composition constant-temperature-line measuring method (JIS H7201) by the constant volume method. The measurement result of such hydrogen storage capacity and Prato flat nature is collectively shown in Table 1.

[0027]

[Table 1]

第4 添加元素成分		Co	Ni	Al	Y	La	Zr	Hf	Nb	Ta	Mn
①	水素吸蔵量(H/M)	0.94	1.00	0.91	1.07	1.07	0.99	1.06		0.91	0.96
	プラトー平坦性	0.55	0.49	0.59	0.57	0.57	0.89	0.77		0.85	0.63
②	水素吸蔵量(H/M)	1.20	1.28	1.20	1.34	1.38	1.27	1.33		1.22	1.24
	プラトー平坦性	0.60	0.52	0.61	0.57	0.59	0.92	0.79		0.88	0.70
③	水素吸蔵量(H/M)	1.10	1.16	1.08	1.24	1.25	1.18	1.25	1.10	1.13	1.14
	プラトー平坦性	0.56	0.50	0.60	0.54	0.56	0.90	0.56	0.97	0.83	0.61
④	水素吸蔵量(H/M)	0.99	1.03	0.96	1.14	1.16	1.07	1.16	0.98	1.02	1.00
	プラトー平坦性	0.53	0.49	0.58	0.53	0.54	0.91	0.54	0.98	0.84	0.57
⑤	水素吸蔵量(H/M)	0.89	0.84	0.87	1.00	0.99	0.94	0.99		0.91	0.93
	プラトー平坦性	0.52	0.49	0.57	0.53	0.55	0.88	0.55		0.83	0.54
⑥	水素吸蔵量(H/M)	0.60	0.57	0.57	0.67	0.69	0.61	0.69		0.61	0.60
	プラトー平坦性	1.23	1.30	1.21	1.05	1.03	1.11	1.03		1.00	1.17

[0028] In the alloy of sample No. \*\* of this invention - \*\*, as an addition of the 4th element, a good value is shown in hydrogen storage capacity and plateau flat nature, and, as for the result of Table 1, hydrogen storage capacity and plateau flat nature show that it is a value lower than the example of this invention about sample No. \*\* with this invention out of range by the 0.5 - 5.0at% thing. About the above-mentioned alloy, the effect of heat treatment over hydrogen \*\*\*\*\* is shown in drawing 17 (a) and 17 (b). the aforementioned \*\*Ti47.5Cr28.5V19.0nickel5.0 \*\*\*\* -- as shown in drawing 17 (a), although the organization is the two phase of BCC+C14 and hydrogen \*\*\*\*\* is a quite low value, before heat treatment, the hydrogen \*\*\*\*\* improves by quenching after 1200 degree-Cx2hr This is considered to be based on the BCC haplosis by heat treatment of this invention. Moreover, as shown in drawing 17 (b), it is \*\*Ti26.2Cr33.2V39.6nickel1.0. The effect then shown in the hydrogen \*\*\*\*\* of heat treatment is small compared with the aforementioned \*\* alloy. In this \*\* alloy, this is before heat treatment, and since it is already BCC single phase, it is considered that heat treatment contributed to the homogeneous effect.

[0029]

[Effect of the Invention] Since according to the hydrogen storing metal alloy of this invention plateau flat nature is further improved with hydrogen \*\*\*\*\* which was excellent with addition of the 4th element and the hysteresis is reduced, when actually using it, while being hard to receive the restrictions by the operating environment and showing the stable equilibrium pressure, the amount of effective [ used ] is further expandable.

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**TECHNICAL FIELD**

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PRIOR ART

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[Description of the Prior Art] From a viewpoint of global environment problems, reuse of solar heat, atomic power, hydraulic power, a wind force, heat of the earth, and waste heat etc. is proposed as new energy replaced with a fossil fuel. However, how in any case, the energy is stored and conveyed poses a common problem. Water is electrolyzed using solar heat or hydraulic power, and the system using the hydrogen obtained by this as an energy medium can be called ultimate clean energy in that a raw material is water and the product which consumes energy and can do it is water again.

[0003] or [ that occlusion of the hydrogen gas of about 1000 times or more of own volume of an alloy is carried out, a hydrogen storing metal alloy can store it as a storage / transportation means of this hydrogen, and the volume density is almost equivalent to a liquid or solid-state hydrogen ] -- or it is more than it LaNi<sub>5</sub> by which the metal of body centered cubic structures (BCC structure is called below), such as V, Nb, Ta, and a Ti-V alloy, is already put in practical use as this hydrogen-absorption material etc. -- AB<sub>5</sub> A type alloy and TiMn<sub>2</sub> etc. -- AB<sub>2</sub> Compared with the type alloy, carrying out occlusion of a lot of hydrogen was known for many years. This is because there are many hydrogen-absorption sites in the crystal lattice and the hydrogen storage capacity by calculation is very as large as H/M=2.0 (alloys, such as Ti, V, etc. which are about 50 atomic weight, about 4.0 wt(s)%) with BCC structure.

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**EFFECT OF THE INVENTION**

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[Effect of the Invention] Since according to the hydrogen storing metal alloy of this invention plateau flat nature is further improved with hydrogen \*\*\*\*\* which was excellent with addition of the 4th element and the hysteresis is reduced, when actually using it, while being hard to receive the restrictions by the operating environment and showing the stable equilibrium pressure, the amount of effective [ used ] is further expandable.

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[Translation done.]

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**TECHNICAL PROBLEM**

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[Problem(s) to be Solved by the Invention] The purpose of this invention is for the addition ratio of Ti, Cr, and V to offer the hydrogen storing metal alloy which examines adding the 4th element into a Ti-Cr-V system alloy, and can carry out flattening of the plateau to it, without changing. Other purposes of this invention consider the composition which can carry out BCC haptosis of the organization of the aforementioned 4 yuan system alloy, and are to the thing of 2 phase mixing zone of C14 and BCC to offer a hydrogen storing metal alloy with the aforementioned flat plateau as BCC haptosis with heat treatment.

[0007] From the concrete data about an improvement of the hydrogen absorption and the emission characteristic in the aforementioned 4 yuan system alloy, plateau flat nature, and a hysteresis, another purpose of this invention is to offer the hydrogen storing metal alloy which can demonstrate a material property to the maximum extent without limiting an operating environment.

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MEANS

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[Means for Solving the Problem] The above-mentioned purpose is a general formula  $Tia Crb Vc Ad$  as atomic ratios  $a, b, c,$  and  $d$ . It is attained by the hydrogen storing metal alloy which is expressed, however is characterized by for  $a+b+c+d=100$  and  $A$  being a kind of an IIb group, and Mn, Co, nickel, Zr, Nb, Hf, Ta and aluminum, or two sorts or more, and being  $14 \leq a \leq 60$ ,  $14 \leq b \leq 60$ ,  $9 \leq c \leq 60$ , and  $0 < d < 8$ .

[0009] Moreover, the above-mentioned purpose is a general formula  $Tia Crb Vc Ad$  as atomic ratios  $a, b, c,$  and  $d$ . It is expressed. However,  $a+b+c+d=100$  and  $A$  are a kind of an IIb group, and Mn, Co, nickel, Zr, Nb, Hf, Ta and aluminum, or two sorts or more, and are the composition field of  $14 \leq a \leq 60$ ,  $14 \leq b \leq 60$ ,  $9 \leq c \leq 25$ , and  $0 < d < 8$ . The crystal structure heats and quenches at 1000-1400 degrees C in the alloy which is BCC(body center cube)+C14 (Laves phase), and it is attained by the hydrogen storing metal alloy characterized by performing heat treatment which carries out haplosis to a BCC phase.

[0010]

[Embodiments of the Invention] In order to have a property as a hydrogen storing metal alloy which was excellent by considering as BCC structure and to improve plateau flat nature while the Ti-Cr-V system which is a BCC metal holds the property of the big hydrogen storage capacity which it has structurally from much old experiments namely, an artificer etc. acquires the knowledge that it is effective that predetermined carries out amount addition of the 4th element, and attains this invention based on this.

[0011] In composition of this invention, it becomes a BCC phase or BCC phase +C14 phase like the after-mentioned. Since it is made to BCC-ize with heat treatment in the case of BCC phase +C14 phase, it heated and quenched at 1000-1400 degrees C (2 hours or more are desirable), and the BCC phase has been formed by performing heat treatment which carries out haplosis to a BCC phase. Consequently, while hydrogen storage capacity is large, plateau flat nature improves by addition of the 4th element, and an alloy with the high amount of effective [ used ] as an alloy is especially obtained by this plateau flat disposition top. From the first, also in the component range of BCC single phase, since an effect is in homogenization, heat-treating is not heat treatment only on a plateau flat disposition, and these improvement effects are discovered simultaneously.

[0012] With the conventional BCC type and a Ti-Cr-V alloy, it cannot but become low weighted solidity, without reaching the property which material has, when the operating environment (temperature, pressure) of an alloy is limited, since an inclination exists in a plateau. It becomes impossible to make the hydrogen which carried out occlusion that occlusion cannot be carried out from this to the amount of hydrogen which an alloy has, and in which occlusion is possible, and at once emit completely.

[0013] Next, the technical feature and the reason for limitation of this invention are explained. The 1st invention made  $A$  a kind of an IIb group, and Mn, Co, nickel, Zr, Nb, Hf, Ta and aluminum, or two sorts or more as the 4th element for these components influencing plateau flat nature greatly like drawing 1. Ce etc. is sufficient, although Y and a lanthanoids are desirable and especially Y and La are desirable in an IIb group. Drawing 1 (a) shows Co to the Ti-Cr-V system, and, as for drawing 1 (b), drawing 1 (c) shows the PCT (hydrogen \*\*\*\*\*) curve at the time of adding [ nickel ] one at each % for aluminum in a Ti-Cr-V system to the Ti-Cr-V system. As it is indicated in drawing 2 as the plateau flat nature of this invention, with Co addition alloy, it is decreasing at 7.5 (L1) degrees to the plateau inclination (L2) of the occlusion line of a base alloy being 13.5 degrees. The value (L1/L2) 7.5 of the ratio in this case / 13.5 = 0.556 is expressed as a relative value of plateau flat nature. On the other hand, expressing with  $Hf = (\text{absorption-pressure force } Pa \text{ in occlusion mean value}) / (\text{desorption pressure force } Pd \text{ in a discharge mean value})$  estimates a hysteresis factor (Hf).

[0014] For example, since plateau flat nature is improved like drawing 1 (b), the amount of effective [ used ] of hydrogen increases. Moreover, a hysteresis can be made small and the amount of repeats of the hydrogen absorption and discharge in the case of actually using it increases from there being few restrictions by the operating

environment and the capacity fully being demonstrated. Drawing 3 summarizes the addition effect (1at%) of the 4th element shown in the below-mentioned example. In this drawing, plateau flat nature and a vertical axis are plotted for a horizontal axis as a hysteresis factor by making the conventional Ti-Cr-V system alloy into a standard. This drawing shows that an effect is large especially from nickel, Co, and Mn as the 4th element.

[0015] As an addition, it is a general formula  $Tia Crb Vc Ad$  as atomic ratios  $a, b, c,$  and  $d$ . It is expressed, however is  $a+b+c+d=100$ . Having specified to  $14 \leq a \leq 60$ ,  $14 \leq b \leq 60$ ,  $9 \leq c \leq 60$ , and  $0 < d < 8$  If  $c$  is  $c \geq 60$ , only by adjustment of a Ti/Cr ratio, it becomes difficult [ plateau oppression \*\* ], and when  $a$  is 60 \*\*, plateau \*\* will fall remarkably, and when  $b$  is 60 \*\*, plateau \*\* will become remarkably high. When  $a$  and  $b$  are furthermore less than 14, respectively, BCC-ization by heat treatment becomes difficult. On the other hand, about  $d$ , when  $d$  is  $d > 8$ , plateau flat nature will deteriorate rather than the original 3 yuan system alloy. Moreover, when  $d$  decreases from 8, the improvement effect of flat nature also becomes small in proportion to it.

[0016] Drawing 4 shows boundary composition of BCC which is the 3 yuan state diagram of a Ti-Cr-V system, and shows the fundamental feature of this invention, and BCC+C14 phase, C14 exists in a Ti-Cr system side, and 2 phase field exists in this circumference. It is necessary to become 2 phase coexistence of BCC+C14 and to carry out BCC haplosis with subsequent heat treatment in [ composition ]  $9 \leq c \leq 25$ , at an atomic ratio. Moreover, in  $c < 9$ , since the haplosis of BCC becomes difficult even if it heat-treats, it has excepted.

[0017] Next, the hydrogen \*\*\*\*\* of this invention hydrogen storing metal alloy is explained. First, like the above, the basic alloy system of this invention is a Ti-Cr-V system, and adds the 4th element to this. Therefore, as a property of an alloy, this fundamental system is inherited and contrast with this can explain. It is surmised by the sludge which deposits in a BCC phase grain boundary decreasing, and promoting BCC-ization by addition of the 4th element of the above, that it has led to the improvement of a hydrogen-desorption property.

[0018] An operation of heat treatment of this invention is considered still as follows. The lattice strain produced in the interface of a two phase as mentioned above changes the distribution state of hydrogenation distortion produced according to hydrogenation. Especially, in the alloy of BCC structure like this invention, distortion produced according to hydrogenation has big influence on hydrogen absorption and the pressure differential (hysteresis) of discharge. In the alloy which has the fine structure like this invention, it becomes possible by controlling such an early distortion by heat treatment to make the optimal small strain distribution of a hysteresis.

[0019] In this invention, heat treatment temperature becomes difficult to get at less than 1000 degrees C, and, on the other hand, in 1400-degree-C \*\*, the effect is heat. Moreover, as heat treatment time, a treatment effect is inadequate in less than 1 minute, and it is 100. It is in the inclination for a treatment effect to be saturated, and \*\*\*\*\* is enough less than [ this ]. Moreover, as cooling processing, it is preferably good at hardening processing. Moreover, solution treatment is homogenization and homonymy, when you may combine with an aging treatment and this aging treatment is not taken. this invention is explained in full detail based on an example below.

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## EXAMPLE

### [Example]

without it changes the Ti/Cr/V ratio of a base alloy on the following conditions as an example of example 1 this invention -- the 4th element X -- 1at% -- as a property [ in / the operating environment (0 degree-C ten atmospheric pressure of hydrogen restoration, 40 degrees-C one atmospheric pressure of hydrogen desorption) of FCEV (fuel cell electric vehicle) / it adds and ] -- hydrogen \*\*\*\*\* -- especially, measurement of plateau flat nature and a hysteresis factor was performed, and structural analysis and the organization were investigated further [0021]

Base alloy composition: Ti26.5Cr33.5V 40.0 sample-offering alloy composition : About 20g ingot performed by the arc dissolution in an argon they are [ dissolution ] Ti26.24 Cr 33.17V39.60Al.00, A=Y, and La, Zr, Hf, Nb, Ta, Mn, Co, nickel and aluminum and for which all the samples of this example used water-cooled copper Haas. All the data of this example ground the ingot [ having cast ] in air, and heat-treated by carrying out Ar enclosure (200 - 300Torr) to a quartz tube (after [ 1200 degree-Cx2hr ] water quenching). As activation, they are 500 degrees C and 10-4torr vacuum length +50atm. After carrying out the four-cycle loop of the hydrogen pressurization and performing it, the hydrogen storage capacity and \*\*\*\*\* of an alloy are performed by the PCT measurement based on the vacuum condition specified for the pressure composition constant-temperature-line measuring method (JIS H7201) by the constant volume method. Moreover, transmission-electron-microscope observation produced the thin film by ion milling from the sample of bulk.

[0022] Moreover, structural analysis of an alloy was performed using EDX (energy-dispersion type X diffraction) of a transmission electron microscope and attachment. The crystal structure model was created based on the information furthermore acquired with the transmission electron microscope, and lied belt analysis of powder X diffraction data was performed. Lied belt analysis can be asked for the weight fraction of each phase by calculation while it can carry out elaboration of the crystal structure parameter using diffraction intensity unlike the usual X-ray diffraction method.

[0023] Analysis soft RIETAN94 which the National Institute for Research in Inorganic Materials spring doctor developed was used for lied belt analysis. Although the phase molar fraction and crystal structure parameter as an average are obtained with a sufficient precision, for the analysis, a fairly probable crystal structure model is required of lied belt analysis. drawing 5 - drawing 14 -- as a measurement result of this example, hydrogen storage capacity is shown in a horizontal axis, and an parallel pressure shows each for a PCT property to a vertical axis here -- drawing 5 -- the aforementioned base alloy and this -- Co1at% -- the property about the added alloy is shown. Similarly, drawing 6 - drawing 14 show each of the PCT curve about what added 1at% of the following nickel, aluminum, Y, La, Zr, Hf, Ta, Mn, and Nb like drawing 5. As compared with the base alloy, improvement in the hydrogen storage capacity as hydrogen \*\*\*\*\* , Prato flat nature, and a hysteresis factor was accepted from these drawings by 4th element 1at% of addition.

[0024] Next, each is shown for the energy-dispersion type X diffraction result used for structural analysis about Co, nickel, and aluminum addition alloy in drawing 15 (a) - (c). The peak which was well in agreement with the peak position peculiar to BCC structure also in the chart of which alloy was accepted. furthermore, the microstructure of a base alloy -- as 100 times of drawing 16 (a), and the 500 time photograph of 16 (b) -- nickel -- 1at% -- the microstructure photograph of the added alloy is shown as 100 times of drawing 16 (c), and a 500 time photograph of 16 (d) By addition of the 4th element, a new organization does not appear at all, but the organization of a base alloy is improved further, and this photograph shows that it is in the inclination which decreases a two phase field.

[0025] Example 2 this example considers change of hydrogen \*\*\*\*\* by composition of an alloy content. the base alloy of a Ti-Cr-V system alloy -- the 4th element -- adding -- A= 0.5 and 1. -- it adjusts to the following component (No. \*\*-\*\*) so that it may become 0, 5.0, and 8.0at(s)%

\*\* Ti15.0Cr34.7V49.8Al0.5 (this invention)  
 \*\* Ti34.7Cr15.0V49.8Al0.5 (this invention)  
 \*\* Ti26.2Cr33.2V39.6Al1.0 (this invention)  
 \*\* Ti47.5Cr28.5V19.0Al5.0 (this invention)  
 \*\* Ti28.5Cr47.5V19.0Al5.0 (this invention)  
 \*\* Ti25.0Cr35.0V32.0Al8.0 (example of comparison : outside of a claim)

[0026] Here, about 20g ingot performed all of A=Co, nickel, aluminum, Y, La, Zr, Hf, Ta and Mn, and the sample of this example by the arc dissolution in an argon which used water-cooled copper Haas. All the data of this example ground the ingot [ having cast ] in air, and heat-treated by carrying out Ar enclosure (200 - 300Torr) to a quartz tube (after [ 1200 degree-Cx2hr ] water quenching). As activation, they are 500 degrees C and 10-4torr vacuum length +50atm. After carrying out the four-cycle loop of the hydrogen pressurization and performing it, the hydrogen storage capacity and \*\*\*\*\* of an alloy are performed by the PCT measurement based on the vacuum condition specified for the pressure composition constant-temperature-line measuring method (JIS H7201) by the constant volume method. The measurement result of such hydrogen storage capacity and Prato flat nature is collectively shown in Table 1.

[0027]

[Table 1]

第4 添加元素成分		Co	Ni	Al	Y	La	Zr	Hf	Nb	Ta	Mn
①	水素吸蔵量(H/M)	0.94	1.00	0.91	1.07	1.07	0.99	1.06		0.91	0.96
	プラトー平坦性	0.55	0.49	0.59	0.57	0.57	0.89	0.77		0.85	0.63
②	水素吸蔵量(H/M)	1.20	1.28	1.20	1.34	1.38	1.27	1.33		1.22	1.24
	プラトー平坦性	0.60	0.52	0.61	0.57	0.59	0.92	0.79		0.88	0.70
③	水素吸蔵量(H/M)	1.10	1.16	1.08	1.24	1.25	1.18	1.25	1.10	1.13	1.14
	プラトー平坦性	0.56	0.50	0.60	0.54	0.56	0.90	0.56	0.97	0.83	0.61
④	水素吸蔵量(H/M)	0.99	1.03	0.96	1.14	1.16	1.07	1.16	0.98	1.02	1.00
	プラトー平坦性	0.53	0.49	0.58	0.53	0.54	0.91	0.54	0.98	0.84	0.57
⑤	水素吸蔵量(H/M)	0.89	0.84	0.87	1.00	0.99	0.94	0.99		0.91	0.93
	プラトー平坦性	0.52	0.49	0.57	0.53	0.55	0.88	0.55		0.83	0.54
⑥	水素吸蔵量(H/M)	0.60	0.57	0.57	0.67	0.69	0.61	0.69		0.61	0.60
	プラトー平坦性	1.23	1.30	1.21	1.05	1.03	1.11	1.03		1.00	1.17

[0028] In the alloy of sample No. \*\* of this invention - \*\*, as an addition of the 4th element, a good value is shown in hydrogen storage capacity and plateau flat nature, and, in hydrogen storage capacity and plateau flat nature, the example of this invention shows that it is a low value about sample No. \*\* with this invention out of range by the 0.5 - 5.0at% thing from the result of Table 1. About the above-mentioned alloy, the effect of heat treatment over hydrogen \*\*\*\*\* is shown in drawing 17 (a) and 17 (b). the aforementioned \*\*Ti47.5Cr28.5V19.0nickel5.0 \*\*\*\* -- as shown in drawing 17 (a), although the organization is the two phase of BCC+C14 and hydrogen \*\*\*\*\* is quite a low value, before heat treatment, the hydrogen \*\*\*\*\* improves by quenching after 1200 degree-Cx2hr This is considered to be based on the BCC haplosis by heat treatment of this invention. Moreover, as shown in drawing 17 (b), it is \*\*Ti26.2Cr33.2V39.6nickel1.0. The effect then shown in the hydrogen \*\*\*\*\* of heat treatment is small compared with the aforementioned \*\* alloy. In this \*\* alloy, this is before heat treatment, and since it is already BCC single phase, it is considered that heat treatment contributed to the homogeneous effect.

[Translation done.]



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**DESCRIPTION OF DRAWINGS**

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**[Brief Description of the Drawings]**

- [Drawing 1] the Ti-Cr-V system alloy and this concerning this invention -- the 4th element -- 1at% -- it is drawing in which showing hydrogen \*\*\*\*\* at the time of adding, and showing (a) Co addition, (b) nickel addition, and (c) aluminum addition
- [Drawing 2] the Ti-Cr-V system alloy and this concerning this invention -- Co1at% -- it is explanatory drawing of the plateau flat nature of the added alloy
- [Drawing 3] It is drawing showing the relation between the plateau flat nature at the time of carrying out various element addition, and a hysteresis factor in the Ti-Cr-V system alloy and this concerning this invention.
- [Drawing 4] It is drawing showing the state diagram of the Ti-Cr-V ternary alloy concerning this invention.
- [Drawing 5] the Ti-Cr-V system alloy and this concerning this invention -- as the 4th element -- Co -- 1at% -- it is drawing showing hydrogen \*\*\*\*\* at the time of adding
- [Drawing 6] the Ti-Cr-V system alloy and this concerning this invention -- as the 4th element -- nickel -- 1at% -- it is drawing showing hydrogen \*\*\*\*\* at the time of adding
- [Drawing 7] the Ti-Cr-V system alloy and this concerning this invention -- as the 4th element -- aluminum -- 1at% -- it is drawing showing hydrogen \*\*\*\*\* at the time of adding
- [Drawing 8] the Ti-Cr-V system alloy and this concerning this invention -- as the 4th element -- Y -- 1at% -- it is drawing showing hydrogen \*\*\*\*\* at the time of adding
- [Drawing 9] the Ti-Cr-V system alloy and this concerning this invention -- as the 4th element -- La -- 1at% -- it is drawing showing hydrogen \*\*\*\*\* at the time of adding
- [Drawing 10] the Ti-Cr-V system alloy and this concerning this invention -- as the 4th element -- Zr -- 1at% -- it is drawing showing hydrogen \*\*\*\*\* at the time of adding
- [Drawing 11] the Ti-Cr-V system alloy and this concerning this invention -- as the 4th element -- Hf -- 1at% -- it is drawing showing hydrogen \*\*\*\*\* at the time of adding
- [Drawing 12] the Ti-Cr-V system alloy and this concerning this invention -- as the 4th element -- Ta -- 1at% -- it is drawing showing hydrogen \*\*\*\*\* at the time of adding
- [Drawing 13] the Ti-Cr-V system alloy and this concerning this invention -- as the 4th element -- Mn -- 1at% -- it is drawing showing hydrogen \*\*\*\*\* at the time of adding
- [Drawing 14] the Ti-Cr-V system alloy and this concerning this invention -- as the 4th element -- Nb -- 1at% -- it is drawing showing hydrogen \*\*\*\*\* at the time of adding
- [Drawing 15] the Ti-Cr-V system alloy concerning this invention -- the 4th element -- 1at% -- it is drawing in which showing the EDX chart at the time of adding, and showing (a) Co addition, (b) nickel addition, and (c) aluminum addition
- [Drawing 16] the Ti-Cr-V system alloy and this concerning this invention -- as the 4th element -- nickel -- 1at% -- the metal texture photograph at the time of adding -- it is -- 100 times of (a) base alloy, 500 times of (b) base alloy, and (c) nickel -- 1at% -- 100 times and (d) nickel which were added -- 1at% -- it is the added 500 time photograph
- [Drawing 17] hydrogen \*\*\*\*\* in the heat treatment order which shows the effect of heat treatment concerning this invention -- an example, (a) Ti47.5Cr28.5V19.0nickel5.0, and (b) Ti26.2Cr33.2V39.6nickel1.0 It is shown drawing.

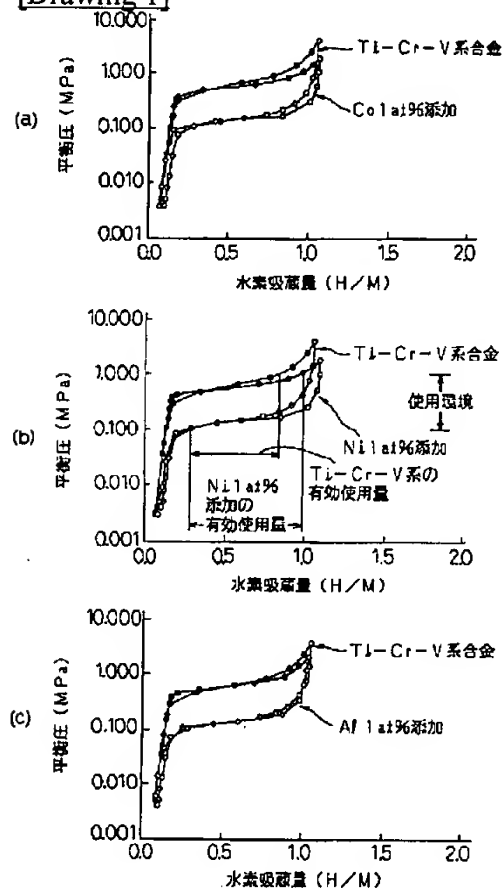
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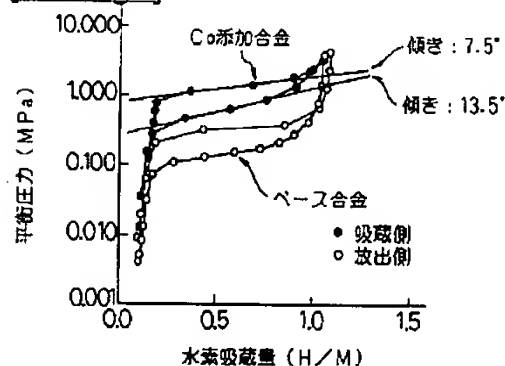
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## DRAWINGS

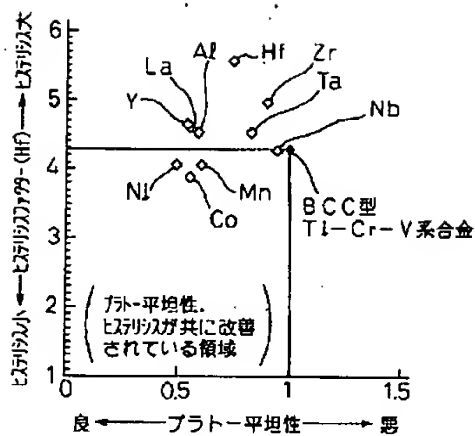
[Drawing 1]



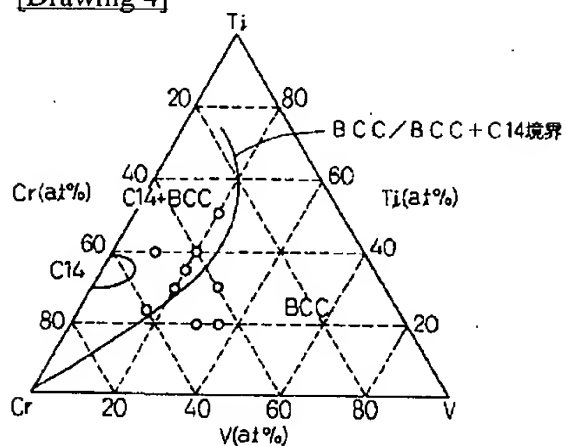
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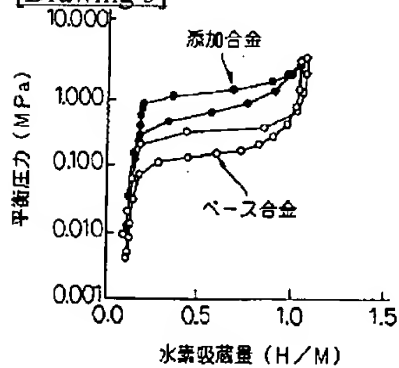
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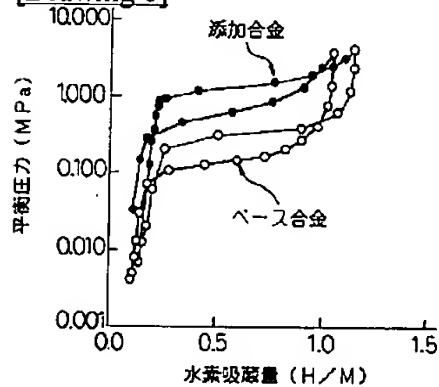
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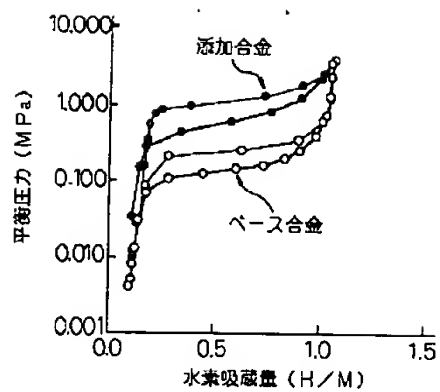
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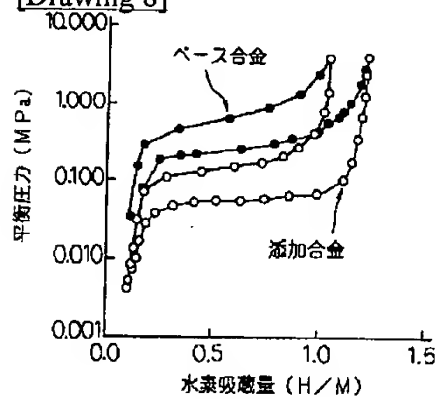
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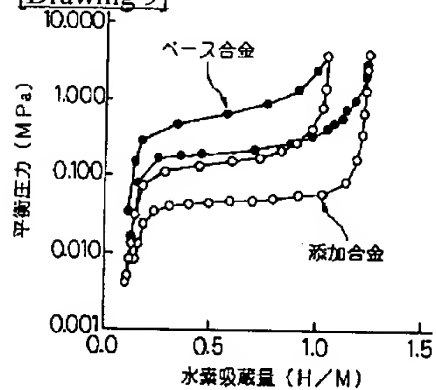
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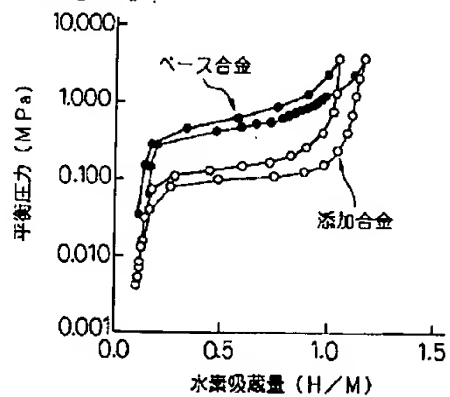
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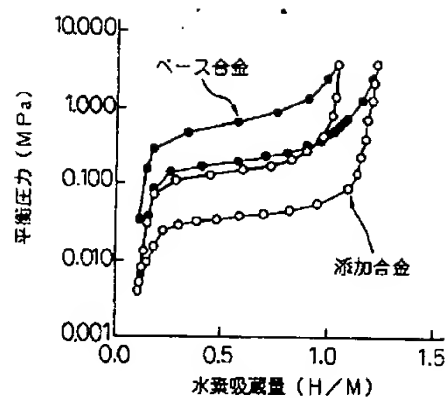
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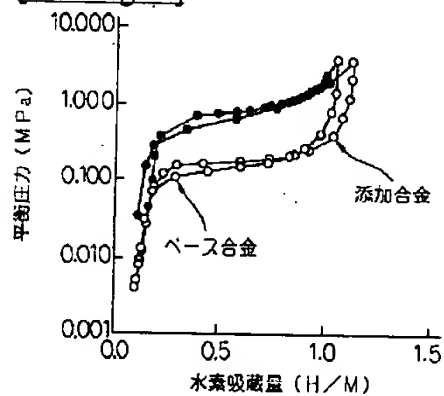
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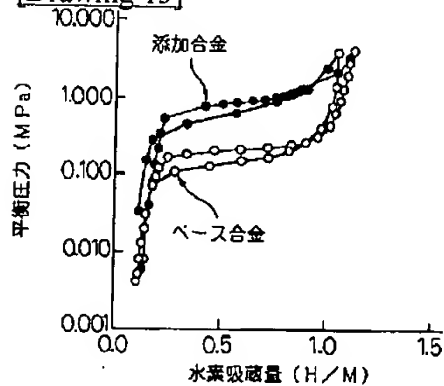
[Drawing 11]



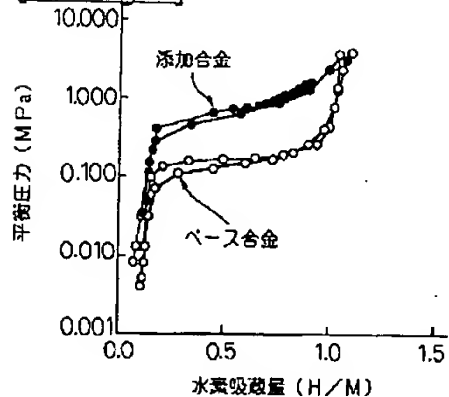
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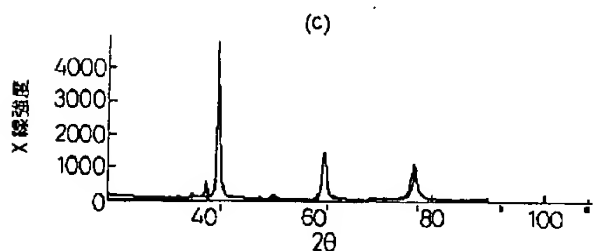
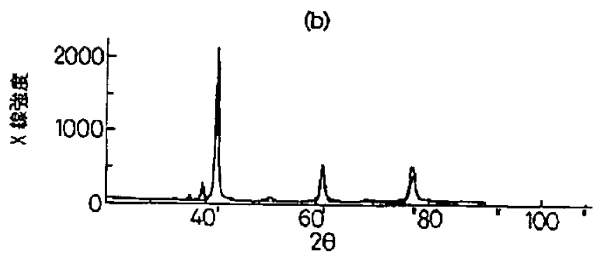
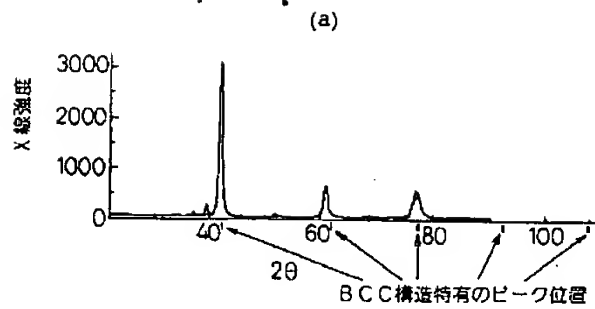
[Drawing 13]



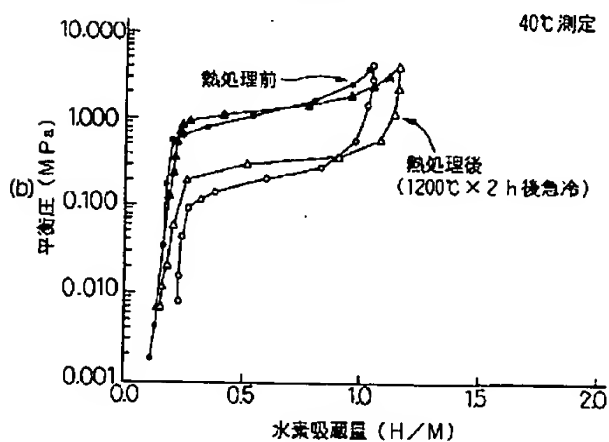
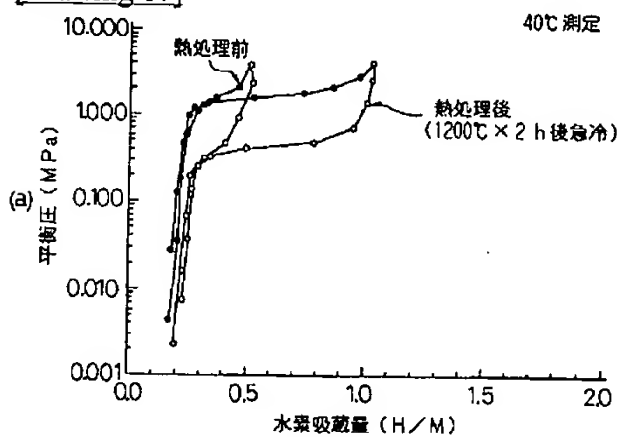
[Drawing 14]



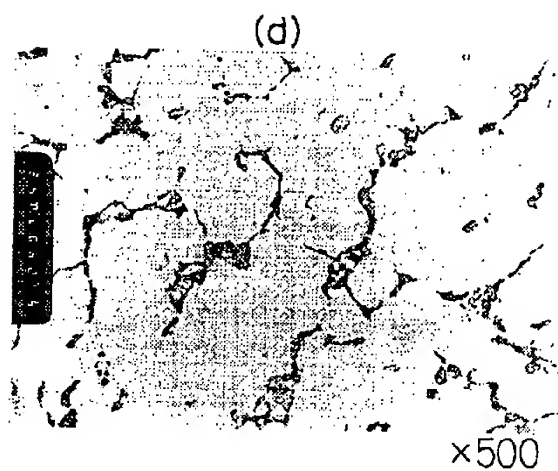
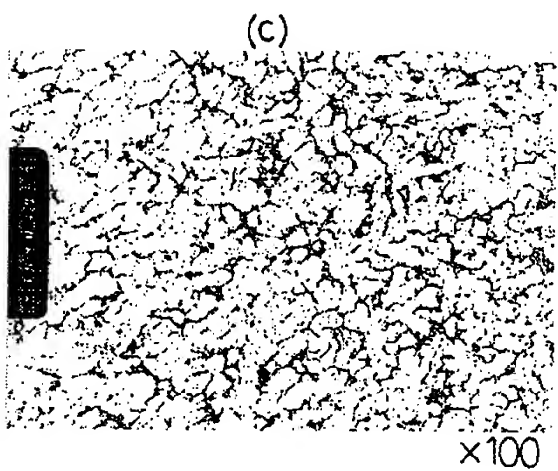
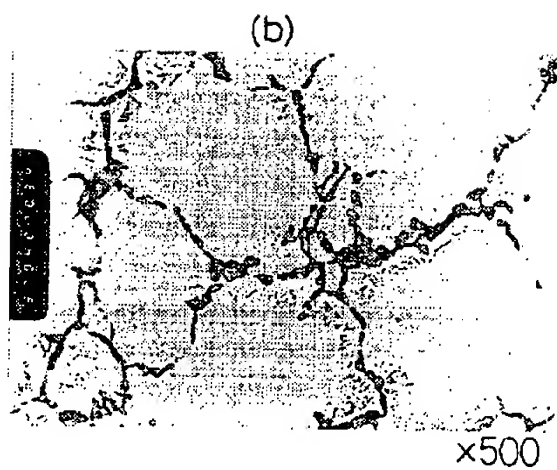
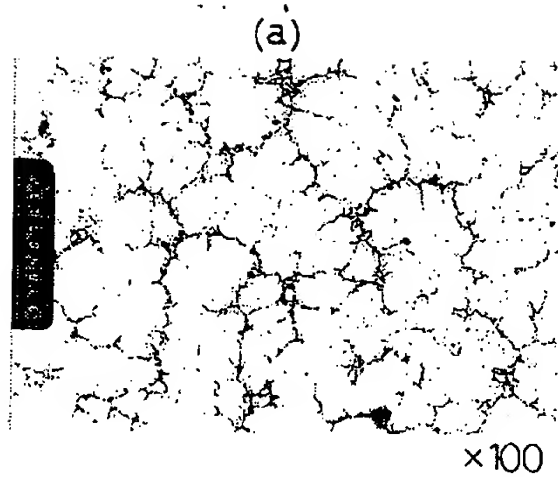
[Drawing 15]



[Drawing 17]



[Drawing 16]



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[Translation done.]